TAbMEP Assessment: ICARTT Propane Measurements

1. Introduction

Here we provide the assessment for the propane (C_3H_8) measurements during the summer 2004 ICARTT field campaign [*Fehsenfeld et al.*, 2006, *Singh et al*., 2006]. The inter-platform assessment is based upon the four wing-tip-to-wing-tip intercomparison flights conducted during the field campaign. The two techniques for the WP-3D are compared using all available data from the mission. Recommendations provided here offer TAbMEP assessed biases for each of the measurements and a systematic approach to unifying the ICARTT propane data for any integrated analysis. These recommendations are directly derived from the instrument performance demonstrated during the ICARTT measurement comparison exercises and are not to be extrapolated beyond this campaign.

2. ICARTT Propane Measurements

Three whole air sampler instruments were deployed on three aircraft. Table 1 summarizes these techniques and gives references for more information.

Table 1. Propane measurements deployed on aircraft during ICARTT

Aircraft	Instrument	Reference
NASA DC-8	Whole Air Sampler (WAS)	*Colman et al.* [2001]
NOAA WP-3D	Whole Air Sampler (WAS) Flame Ionization Detection (FID)	Contact PI: eatlas@rsmas.miami.edu
	Whole Air Sampler (WAS) Mass Spectrometer Detection (MSD)	Contact PI: eatlas@rsmas.miami.edu
FAAM BAe-146	Whole Air Sampler (WAS)	*Hopkins et al.* [2003]

3. Summary of Results

Table 2 summarizes the assessed biases as well as PI reported uncertainties for each of the four propane measurements involved in the intercomparisons. More detailed descriptions are provided to illustrate the process for the bias assessment in Section 4.1. The TAbMEP-prescribed IEIP procedures cannot be applied to the ICARTT propane measurements for precision assessment. This is because the reported data have large time gaps and a small data population (see Section 3.1 of the introduction). The assessed bias reported in Table 2 (see Section 4.1 for details) can be applied to maximize the consistency between the data sets, by subtracting the value from the reported data to 'unify' the data sets. If one assumes instrument performance remained constant throughout the mission, the assessed bias may be extrapolated to the entire mission although it is derived from intercomparison periods only.

Table 2. Recommended ICARTT Propane measurement treatment

Aircraft/Instrument	Reported 2σ Uncertainty	Assessed Bias (pptv)
NASA DC-8 WAS	10%	$-7.465 - 0.0222\ C_3H_{8\ DC\text{-}8}$
NOAA WP-3D WAS FID	10%	$12.65 - 0.0621\ C_3H_{8\ FID}$
NOAA WP-3D WAS MSD	10%	$12.33 - 0.0601\ C_3H_{8\ MSD}$
FAAM BAe-146 WAS	Point by Point, average: 32%[a]	$-7.830 + 0.138\ C_3H_{8\ BAe\text{-}146}$

[a] The average encompasses only the comparison period for DC-8/BAe-146.

Figures 1 a and b display the PI reported uncertainties and recommended biases for the four propane instruments.

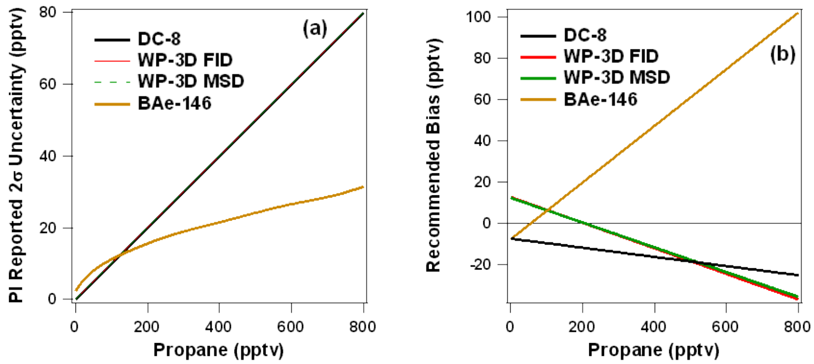

Figure 1. PI reported 2σ uncertainty (panel a) and recommended bias (panel b) for DC-8 (black), WP-3D FID (red), WP-3D MSD (green), and BAe-146 (gold) as a function of propane level. Values were calculated based upon data shown in Table 2. The BAe-146 PI reported uncertainty was calculated using a function derived from the 60 second merge file.

4. Results and Discussion

4.1 Bias Analysis

Section 3.3 in the introduction describes the process used to determine the best estimate bias. Figures 2 and 4 show the time series plots for the DC-8/WP-3D and DC-8/BAe-146 comparisons. The DC-8 is consistently lower than both WP-3D and BAe-146 by 13 pptv and 4 pptv on average respectively. The two techniques used on the WP-3D were compared for all flights using the WAS merge file, shown in Figure 5. On average the FID data were less than 0.5 pptv larger than the MSD data. Figures 6 – 9 show the magnitude of the bias for each intercomparison and Figures 10 – 13 show the corresponding relative residuals.

For 2 of the 3 DC-8/WP-3D flights, there are only 3 or 4 overlapping points with a small range of variation (less than 100 pptv). It is not statistically significant to show the linear regression for these flights. Therefore, linear regression is performed over the data combined from all three DC-8/WP-3D flights. The linear relationships listed in Table 3 were derived from the regression equations found in Figures 3 and 4. The regression equations are expressed as a function of C_3H_8 DC-8 shown in Table 3. The reference standard for comparison (RSC), as defined in the introduction, is constructed by a weighted average of the DC-8, both WP-3D techniques, and the BAe-146. The PI consensus was to give the DC-8 a weight of 2, the FID technique 1.5, the MSD technique 0.5, and the BAe-146 one. (i.e. [2DC-8 + 1.5FID + 0.5MSD + BAe-146]/5) The resulting RSC can be expressed as a function of the DC-8 C_3H_8 measurements as the following:

$$RSC_{C3H8} = 7.465 + 1.022\, C_3H_{8\text{-}DC8}$$

The RSC is then used to calculate the best estimate bias as described in Section 3.3 of the introduction. It should be noted that the initial choice of the reference instrument (DC-8 WAS) is arbitrary, and has no impact on the final recommendations. Table 3 summarizes the assessed measurement bias for each of the four ICARTT propane measurements. Note that additional decimal places were carried in the calculations to ensure better precision. It is also noted that the intercept in the equations listed in Table 3 should not be viewed as an offset. These linear equations are used to best describe the linear relation between the measurements.

The WAS technique for measuring VOCs presents some challenges in analyzing the data. The DC-8 data have an integration time of approximately 60-70 seconds, while the WP-3D data have an integration time between 6-11 seconds. For these measurements to be considered simultaneous and correlated, the start and stop times of the WP-3D data must fall within the start and stop times of the DC-8 data. In order to maximize the data coverage for statistical analysis, one exception is made to this rule. If the shorter (WP-3D) integration time falls outside the longer integration time by no more than two seconds, the data points are also considered to be simultaneous. BAe-146 integration times range from approximately 30-60 seconds. Since the DC-8 and BAe-146 have similar integration times, the measurements are considered correlated if the midpoint of DC-8 or BAe-146 fall within the start and stop time of the other measurement. Only the PI reported data are used in this assessment, and no interpolation is included. It is noted here the integration time difference may potentially be another factor leading to the difference between measurements.

Table 3. ICARTT Propane bias estimates

Aircraft/ Instrument	**Linear Relationships**	**Best Estimate Bias ($a + b\ C_3H_8$) (pptv)**
NASA DC-8 WAS	$C_3H_{8\ DC\text{-}8} = 0.00 + 1.000\ C_3H_{8\ DC\text{-}8}$	$-7.465 - 0.0222\ C_3H_{8\ DC\text{-}8}$
NOAA WP-3D WAS FID	$C_3H_{8\ WP\text{-}3D} = 18.9 + 0.962\ C_3H_{8\ DC\text{-}8}$	$12.65 - 0.0621\ C_3H_{8\ FID}$
NOAA WP-3D WAS MSD	$C_3H_{8\ WP\text{-}3D} = 18.7 + 0.964\ C_3H_{8\ DC\text{-}8}$	$12.33 - 0.0601\ C_3H_{8\ MSD}$
FAAM BAe-146 WAS	$C_3H_{8\ BAe\text{-}146} = -0.423 + 1.19\ C_3H_{8\ DC\text{-}8}$	$-7.830 + 0.138\ C_3H_{8\ BAe\text{-}146}$

As a part of ICARTT intercomparison standard exchange exercises, University of California, Irvine (UCI) prepared the common VOC samples that were sent to University of Miami (Miami), University of New Hampshire (UNH), and University of York (York) for their lab analyses. Some of these same institutions had instruments on the following planes during ICARTT: UCI on the DC-8, Miami on the WP-3D, and York on the BAe-146. The comparison incorporated 9 species, which included propane. We believe that the inclusion of this comparison result will help the readers better understand the airborne intercomparison analysis. The difference in this lab comparison between the DC-8 and WP-3D instruments was 3 pptv, WP-3D being higher, with a DC-8 instrument reading of 1427 pptv. From the same lab comparison, the difference between the DC-8 and BAe-146 was 12 pptv, DC-8 being higher. Comparing the ICARTT flights to this lab comparison shows slightly different relationships for both the DC-8/WP-3D and the DC-8/BAe-146 intercomparisons. The average lab comparison level of 1424 pptv is much higher than levels experience during the intercomparison flights which range from approximately 0 to 800 pptv. Also, the intercomparison flights do not provide a large number of data points for comparison. These are possible contributions to the difference between the lab comparison and the intercomparison flights.

4.2 Precision Analysis

A detailed description of the precision assessment is given in Section 3.1 of the introduction. The IEIP precision, expected variability, and adjusted precision could not be calculated for propane because of the small number of points and large time gaps between measurements.

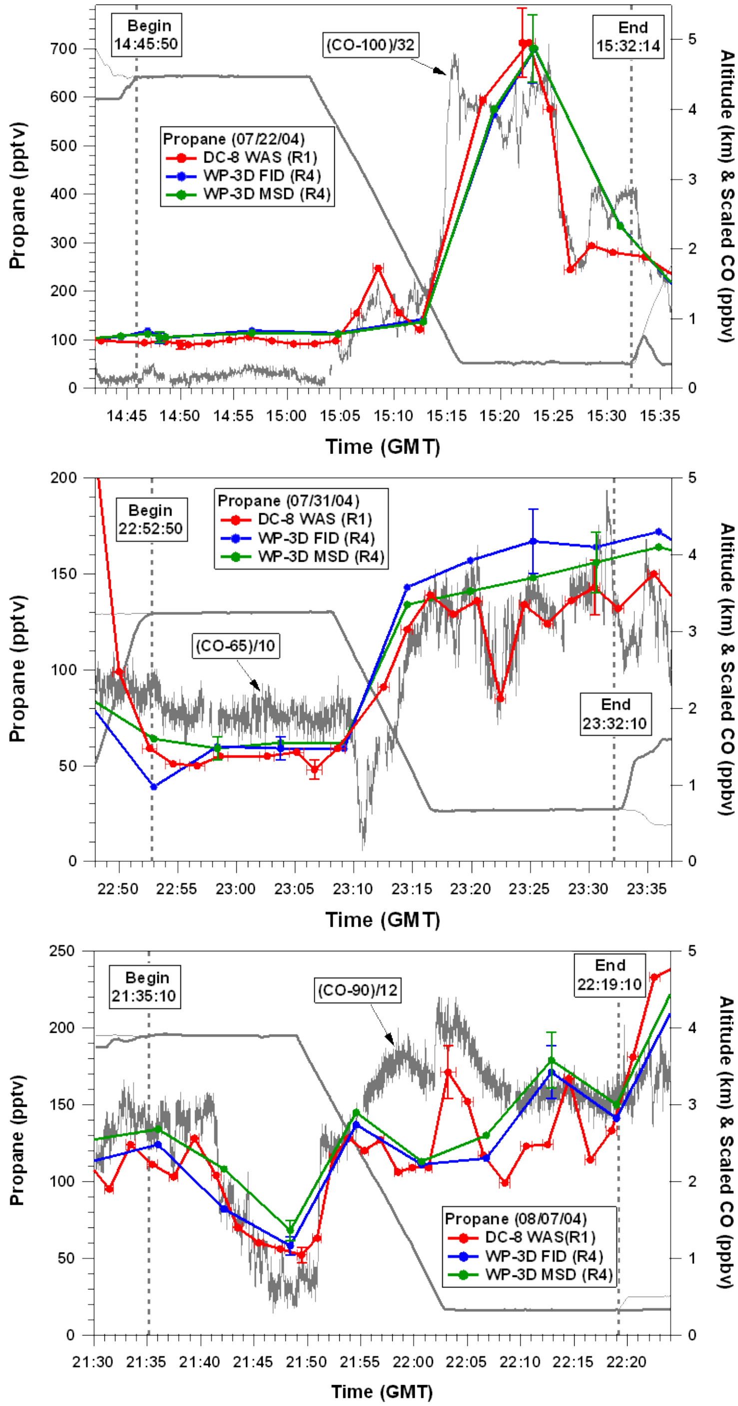

Figure 2. Time series of propane measurements and aircraft altitudes from two aircraft on the three intercomparison flights between the NASA DC-8 and the NOAA WP-3D. Error bars represent the PI reported uncertainty. In parenthesis next to the plane is the data version number.

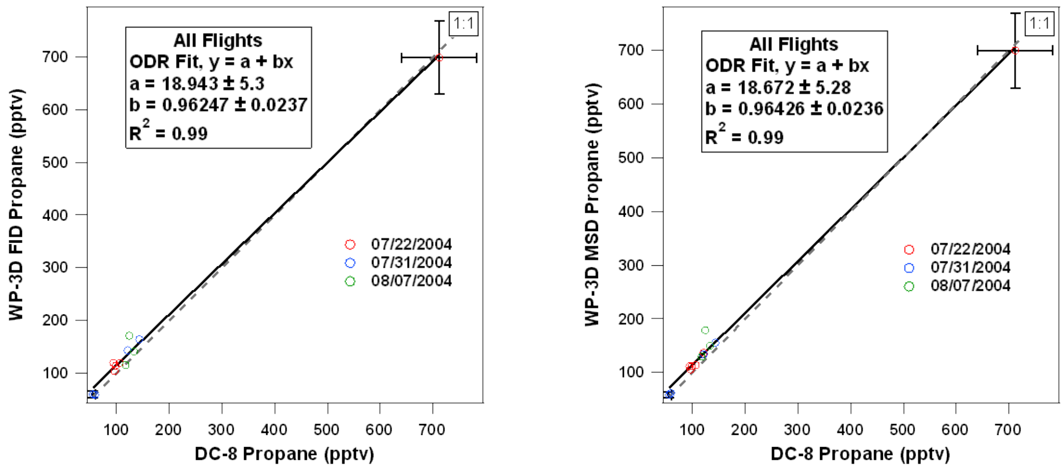

Figure 3. Combined correlation for the propane measurements on NASA DC-8 and the NOAA WP-3D for 7/22, 7/31, and 8/07 2004. (left panel) WP-3D FID and (right panel) WP-3D MSD. Error bars represent the PI reported uncertainty.

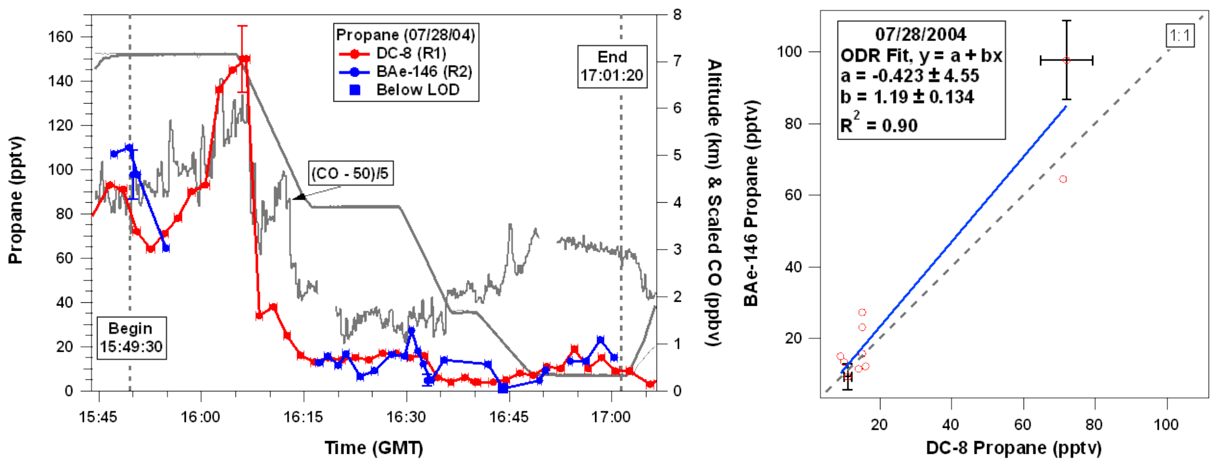

Figure 4. (left panel) Time series of propane measurements and aircraft altitudes from the intercomparison flight between the NASA DC-8 and the FAAM BAe-146. In parenthesis next to the plane is the data version number. (right panel) Correlation between the propane measurements on the two aircraft. Error bars represent the PI reported uncertainty.

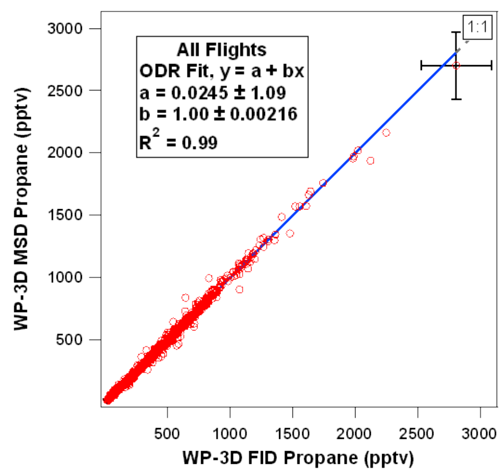

Figure 5. Correlation of WP-3D FID and MSD propane measurements for all ICARTT flights. Data taken from the WAS merge file.

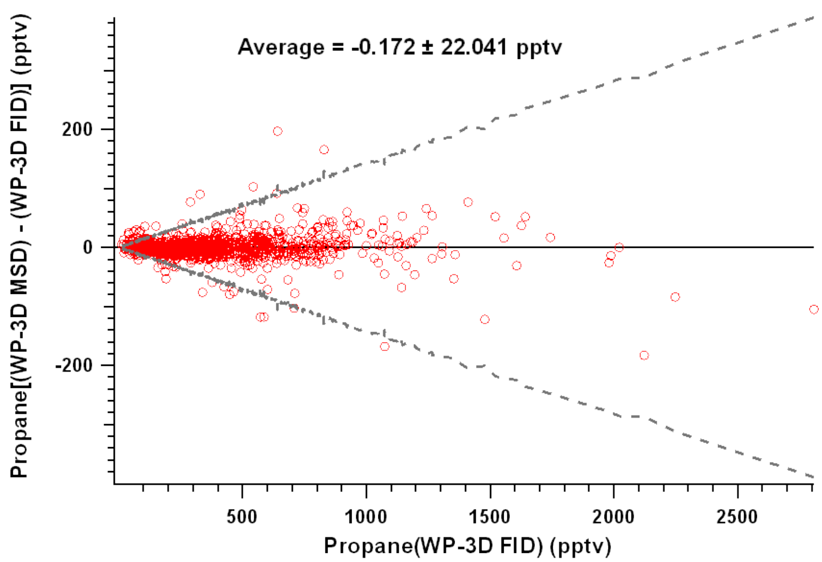

Figure 6. Difference between propane measurements from WP-3D FID and WP-3D MSD for all flights as a function of WP-3D FID propane. The dashed lines indicate the range of results expected from the reported 2σ measurement uncertainties.

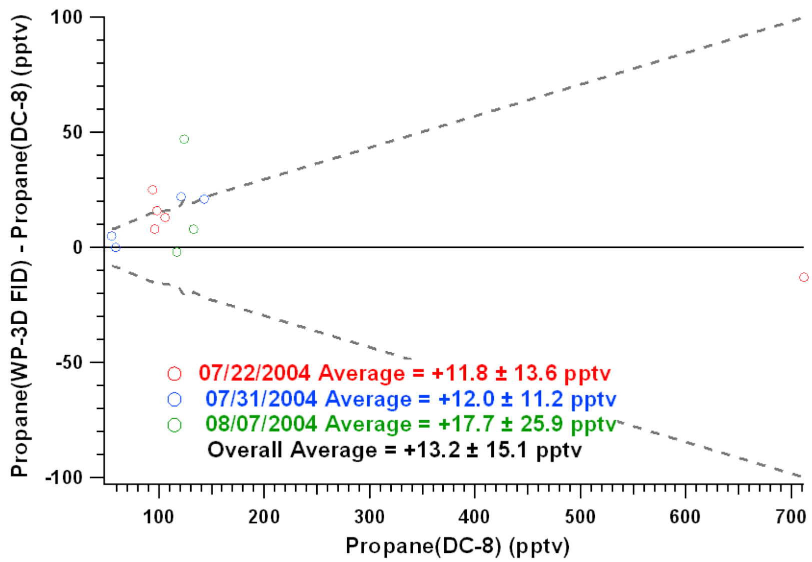

Figure 7. Difference between propane measurements from the three DC-8/WP-3D FID intercomparison flights as a function of DC-8 propane. The dashed lines indicate the range of results expected from the reported 2σ measurement uncertainties.

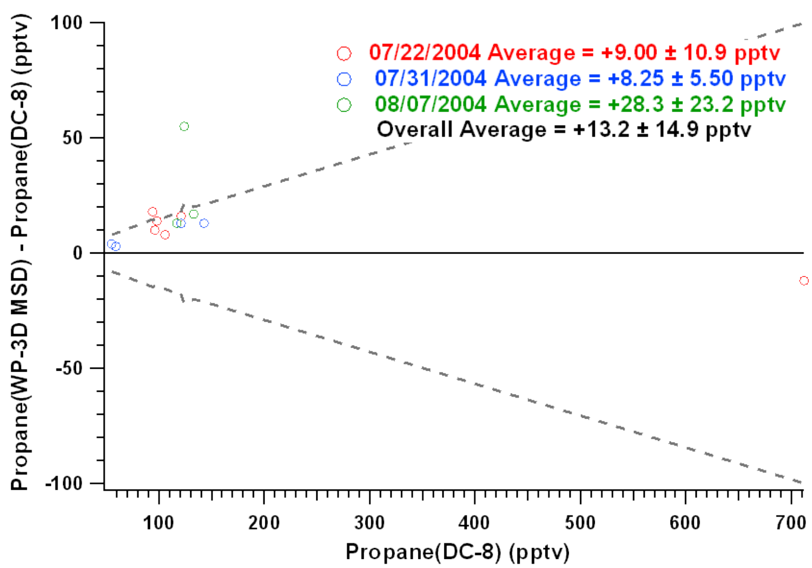

Figure 8. Difference between propane measurements from the three DC-8/WP-3D MSD intercomparison flights as a function of DC-8 propane. The dashed lines indicate the range of results expected from the reported 2σ measurement uncertainties.

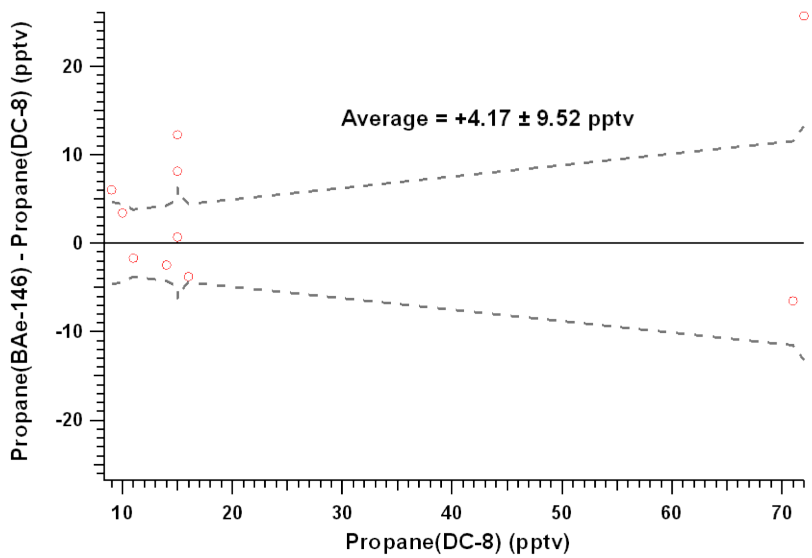

Figure 9. Difference between propane measurements from the DC-8/BAe-146 intercomparison flight as a function of DC-8 propane. The dashed lines indicate the range of results expected from the reported 2σ measurement uncertainties.

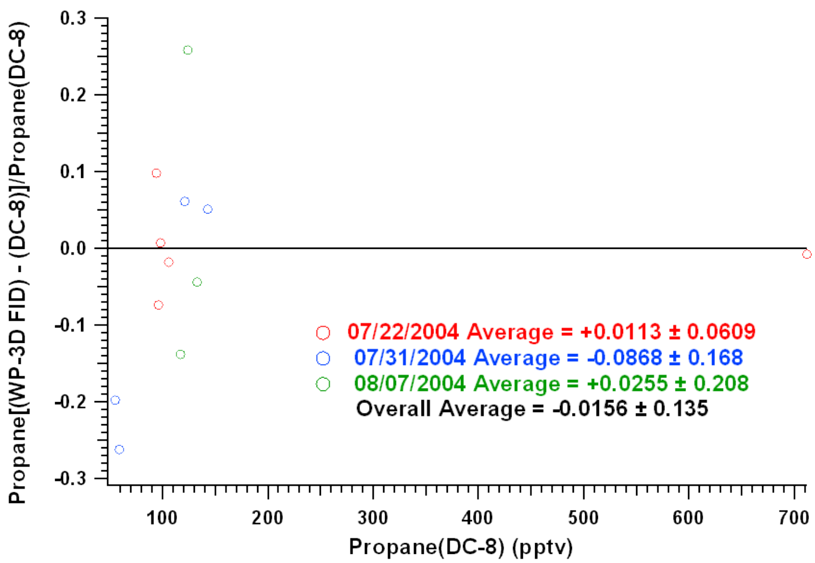

Figure 10. Relative difference between propane measurements from the three DC-8/WP-3D FID intercomparison flights as a function of DC-8 propane. A correction was made to account for bias.

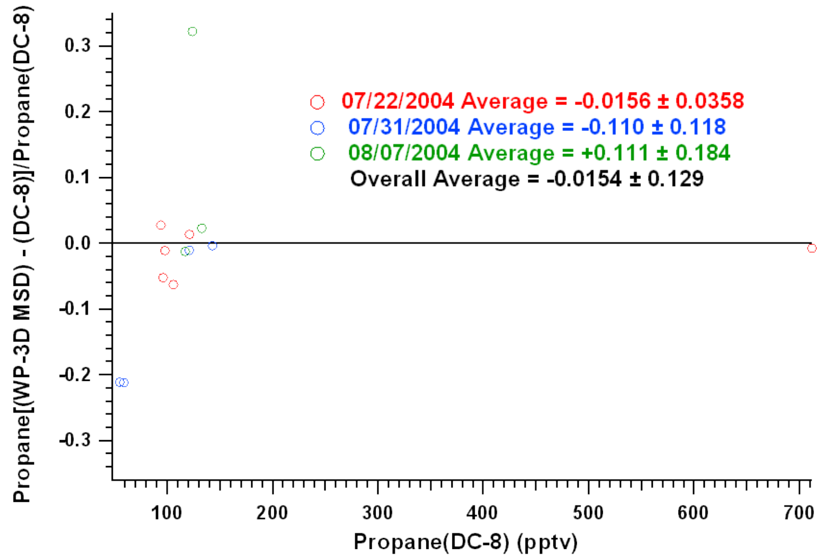

Figure 11. Relative difference between propane measurements from the three DC-8/WP-3D MSD intercomparison flights as a function of DC-8 propane. A correction was made to account for bias.

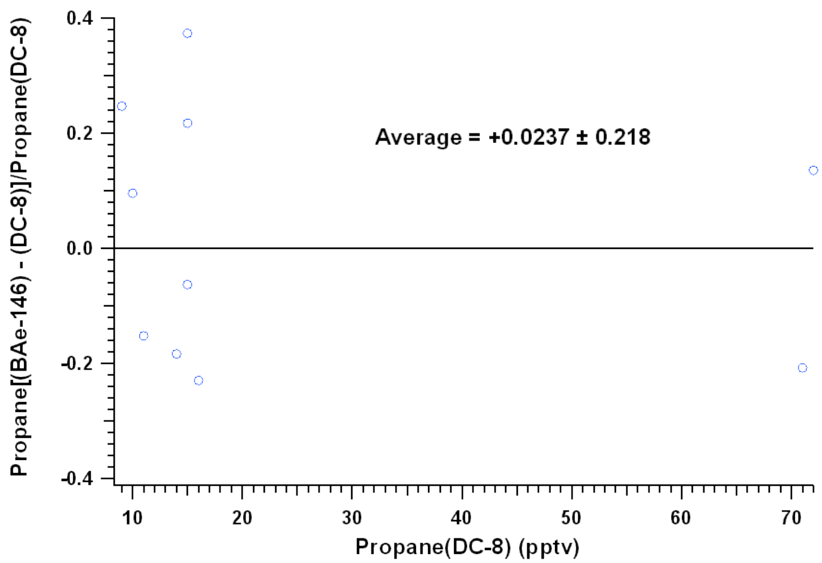

Figure 12. Relative difference between propane measurements from the DC-8/BAe-146 intercomparison flight as a function of DC-8 propane. A correction was made to account for bias.

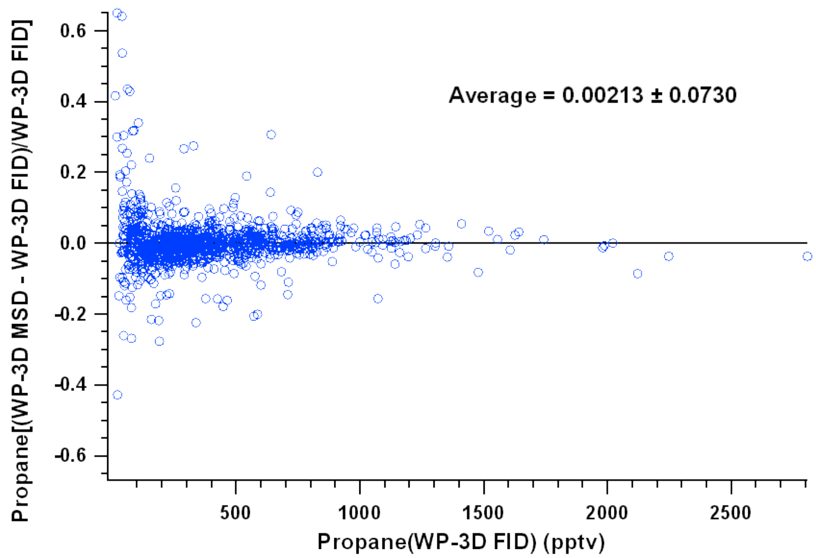

Figure 13. Relative difference between propane measurements from WP-3D FID and WP-3D MSD for all flights as a function of WP-3D FID propane.

References

Colman, J.J., et al. (2001), Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem* ., 73, 3723-3731.

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